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editorial

Nobody's Laughing At Brendan Now

"I went to work the other day," related a friend of mine, "and I said: 'Did you hear the story of the four Irishmen that sailed across the Atlantic in a leather boat?' Everyone waited for the punch line!"

They may have laughed at Tim Severin when he conceived the construction of a leather currach to trace the route of St. Brendan, but everyone who has heard the story of the amazing craft has changed his laughter to admiration (see page 10.)

While the persistence and heroism of Severin and his four crew members deserve loud applause, the world's leather industry can take justifiable pride in the performance of this unusual craft. While we cannot expect that the world's boat builders will suddenly drop the use of wood, fiberglass or steel in favor of leather, the "Brendan" did show that leather is a remarkable substance with remarkable properties for anyone who has the imagination to utilize them.

The story of the "Brendan" makes people realize that leather is an ancient product with centuries of tradition. The "Brendan" has captured the imagination of all those who have heard it. The story will continue to be told again and again. It will be told in next December's **National Geographic**, in excerpts in **Reader's Digest** next Spring, in a full length book release next May, in two fifty-minute television productions due for release some time next year. It will also be told wherever the boat is displayed. Current plans call for its exposition at Boston's **Museum of Science,** Washington's **Explorers Hall,** a shopping center in Peabody, Mass., and at Atlantic City's Convention Hall during the Footwear Manufacturing Conference and Exposition.

The "Brendan" is a story that will be before the public's eye for many months to come, and if the "Brendan" is before the public's eye, then leather is before the public's eye. The leather industry has a great opportunity to promote leather as a marvelous up-to-date product to be used with imagination. Let's hope the industry takes full advantage of the opportunity.

in this issue

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Hides and Leather Research at The Eastern Regional Research Center, USDA

EDWARD M. FILACHIONE
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Introduction

The Eastern Regional Research Center is one of five regional research centers of the Agricultural Research Service, an Agency of the USDA. These centers are responsible for conducting basic and applied research with the objective of finding new and wider uses for American farm commodities. The Hides and Leather Laboratory, one of the seven laboratories at the Eastern Center, conducts research on hides and skins, commodities of the livestock farmer. Fifteen scientists in this laboratory, with some support personnel from the other laboratories, contribute to the research effort in this field. Their mission is to maintain or enhance the utilization of animal hides and skins in any applications that can be visualized.

Practically all animal hides and skins, are by-products of the meat industry and have traditionally been tanned into leather. Because this has been such a profitable outlet for this commodity, our research has been oriented toward leather as a product from hides and skins.

I would like to present briefly some of our recent and current research as it relates to hides, hide processing, pollution, new leathers, and new uses for hides.

Defects:

Hide and skin defects generally exist on the live animal prior to slaughter. Hide defects, the most important source of non-uniformity in leather, downgrade the leather and pose economic problems in shoe manufacturing. Some of the non-uniformity results from scar tissue on the grain surface. Barbed wire and briar scratches may never be eliminated. Hide damage caused by branding has always been a serious economic problem in the tanning industry. This can be minimized by freezebranding, whereby a branding iron chilled in dry ice or liquid nitrogen and then applied to an animal's skin destoys the epidermal pigment cells and causes the new hair to grow in white (1,2). Buffing the leather can correct a major portion of the minimal grain damage (3,4). Disadvantages of freezebranding are: added cost of this new technique, and it is not legally recognized in a number of western states as a means of identifying cattle. Freezebranding has been accepted in Denmark and Norway where about one-third of the cattle are freezebranded. In the U.S. this method of identification has been used by the Arabian horse registry. We believe that adoption of this technique would benefit the leather industry; however, there does not seem to be enough incentive for the livestock industry to use it.

Another defect that has given tanners headaches is known in the trade as "pulpy butt" or "verical fiber." This defect is characterized by a vertical arrangement of the fiber bundles in sections of the corium in contrast to the normal randomly interwoven structure. Upper leather made from such defective hides can be recognized by pulpy texture and inferior strength (5). In the shoe factory such leather fails to withstand the lasting operation. Recent studies at our laboratory and the Tanners' Council Laboratory indicated that the defect is inherent in the hide. Such hides have a high fat content, and the weakness occurs in small areas of the hides, usually the kidney area. This defect is found most often in thick, heavy Hereford hides, (6,7,8). A biopsy study of twin cattle gave strong evidence that this defect is genetically controlled (9,10). Selective breeding could eventually eliminate it.

Such defective hides, although not suitable for shoe upper leather, are perfectly satisfactory for sole leather. Thus, we felt it was desirable to develop a practical, rapid, non-destructive test method to detect vertical fiber defect so as to channel such hides into the proper leather. We developed a needle penetrometer that satisfactorily detects vertical fiber defect in split stock; however, for full thickness hides it needs to be improved (11).

Cockle is a seasonal sheepskin defect that consists of a scattering of dense brownish nodules in the grain layer of sheepskin that seriously downgrades both grain and suede types of leather. Its cause was unknown until our research revealed that the common sheep ked **(Melophagus ovinus)** was responsible for cockle (12,13). Eradication of this ked should be a simple matter provided there is incentive for application of known treatments, a rotenone dip being generally recommended. Work at our laboratory demonstrated that ked infestation resulted in lower value of the three sheep commodities: meat, wool, and skins from infested sheep (14).

Demodective mange, on the other hand, presents a different problem. The cause is known but no means of control is available. Other studies indicate that the mites responsible for this defect are not readily transmitted by direct body contact between animals in feed lots.

We also conducted studies to determine whether blood sucking insects cause grain damage. There was no evidence that stable fly, barn fly, horse fly, or one mosquito variety caused any detectable grain damage.

Recently we undertook studies to learn more about the grain layer. We wanted to know the influence of animal factors such as breed, age, and sex on the grain layer thickness and total thickness of fresh cattle hides, important factors in splitting practice and leather strength, and the effect of processing to wet blue and crust on these thickness characteristics. The grain layer was considered to extend to the junction of the grain and corium and is delineated by the base of the hair roots. Preliminary study (15) indicates the following conclusions:

1. Hereford hides tend to be thicker and have a slightly deeper grain layer than Holsteins of comparable age and sex. Reciprocal crossbreds tend to resemble the sire's breed.

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2. Total thickness increases rapidly with age up to one year, with little change thereafter.

3. Grain depth changes rapidly up to six months, very slowly thereafter.

4. Grain depth increases from about 1.6 mm in fresh rawstock to about 1.0 mm in wet blue to about 0.7 mm in crust.

5. It appeared that the nature of the retannage had an effect on grain depth in the crust.

Preservation:

Because of the perishable nature of hides and skins, they must receive some treatment almost immediately after take-off. About 12 years ago we reported (16) that certain cationic surface active agents, also known as sanitizers, were effective for the short term preservation of hides and skins. These cationic agents are tetrasubstituted ammonium chloride derivatives known as quaternary ammonium chlorides and generally contain one long chain alkyl group of 12, 14, 16, or 18 carbon atoms, two methyl groups and one benzyl group. Use of these materials termed "benzalkonium chlorides, permitted short term preservation of hides for 3-5 days, without damage by microbial attack. A short term preservation should be attractive to the hide processing industry because of certain current trends or practices. These are:

1. The trend to fleshing and demanuring at the packers' level.
2. Collection of hides and skins from small operators.
3. Hauling raw hides to a central curing plant.
4. Hauling raw hides to a tannery for immediate processing, bypassing curing.
5. Processing fresh hides to the blue chrome-tanned stage as a marketable raw material for tanners.
6. Elimination of salt curing and thus avoidance of salt as a pollutant in hide processing.

A short term preservative would provide the packer, hide broker, or tanner a safety factor against delays due to mechanical breakdown, short labor, long haulings, holidays, or other unforeseen factors.

Our laboratory findings were extended by practical tests (by Cliff Benrud (17) of S. B. Foot Tanning Company) that showed that the benzalkonium chloride

(BAC) was taken up very rapidly by the hide. An efficient method of application is to spray the hides with a dilute solution of the benzalkonium chloride in a hide washer. About one ounce of BAC on a 100% active basis is needed per hide, which is of the order of 0.1% of the fresh hide weight. Perhaps slightly more (about 1.5 ounces) would be called for as a safety factor. Because of the small amount needed, the material cost for this preservation treatment is relatively low. On the basis of $1.50 per pound for the benzalkonium chloride (100% active basis), this treatment would cost roughly 14 cents per hide. This is more than offset by savings in salt and avoidance of salt pollution. Furthermore, the benzalkonium chlorides have been registered by EPA as acceptable for this use and offer no pollution problem. They may be used commercially at the packing house level for preserving hides (up to five days), principally for hauling to a tannery for immediate processing or to a curing plant. Hides treated in this way produced satisfactory leather even after five days of storage. Incidentally, our studies showed salt in curing (16).

Seeking further means of preservation without salt, beyond benzalkonium chlorides, we found that relatively low amounts of sodium sulfite or bisulfite with an acid preferably acetic, gave very promising results (18,19). Fleshed and demanured hides treated with about 1-2% of each of these preservatives have been stored up to 28 days without noticeable growth of microorganisms or deterioration. Freshly flayed hides were a more difficult substrate to preserve, however. Satisfactory preservation was noted for at least seven days. We are continuing our studies on sulfite preservation and have conducted some practical tests to evaluate the leathers that result from tanning stock preserved in this manner. Promising results have been obtained with shoe upper leather, shoe lining leather, and cowhide garment leather (20,21). In cooperation with our laboratory, several hide processors and tanners in the U.S. and Canada are evaluating the sulfite-acetic acid preservation process. We feel confident that a short term preservation with this system has been demonstrated. Long term preservation remains to be established.

Another alternative to curing with salt is immediate processing of fresh hides to a marketable stable form. Our laboratory cooperated with a tanner in a study that evaluated the leather made from fresh versus salt-cured hides (22). Evaluation was made in the blue and the crust. In general, the leather made from the fresh hides was equal to or slightly better than that from the salt-cured hides as regards to yield, chrome content, strength, and quality of the leather. Furthermore, processing fresh hides bypasses the salt pollution problem inherent in salted hides. I believe that tanners have considerable expecerience in immediate processing of fresh hides prepared for a short haud by a cold water wash. Marketing wet blue stock in place of cured hides offers considerable economic advantages.

Pollution:

We are also doing some research on control of environmental pollution by hide processors and tanners. Our studies have been concentrated on unhairing effluents because of the large pollutant load of this tannery waste. A moderate size tannery using a paddle vat, hairpulping process, sewers about 20,000 gallons of unhairing effluent daily. This contains about 22,000 ppm BOD, 34,000 ppm suspended solids, 3,500 ppm sulfide, and 4,500 ppm organic nitrogen mainly protein. Our objecttives are major reductions in suspended solids, BOD, and sulfides and the recovery of protein from this effluent. We also hope that some of the products obtained may have value to offset in part the cost of treatment.

An effective procedure was developed for flocculating and removing suspended solids from tannery unhairing effluents under highly alkaline conditions. Good results were obtained by adding an anionic polyeletrolyte (Primafloc A-10) followed by a cationic polyelectrolyte (Primafloc C-3) and sodium hexametaphosphate 23). Large particles formed and settled rapidly and reduced suspended solids by about 90%. This system was satisfactory for a hair pulping, paddle vat effluent but not for a hide processor effluent. However, an anionic polyelectrolyte was found to be effective for the latter system (24). The type of hair pulping process is important as far as flocculation of suspended solids is concerned. The wide variety of flocculating agents available leads us to believe that suitable systems can be developed to effectively remove suspended solids from an effluent as a primary treatment. Because of the high lime content and absence of toxic metals, this sludge may have value as an ingredient of layer rations for poultry feed (25).

Activated sludge was acclimated to unhairing waste by periodic feeding with increasing in-that salt preservation is markedly improved by using benzalkonium chloride as an adjunct to crements of tannery waste. This bio-oxidation process effectively reduced the organic nitrogen and sulfide concentrations in the unhairing effluent by about 90% (26). The sludge was free of heavy metal contamination and had a high lime and protein content. It may find use as an ingredient in poultry feed or perhaps in fertilizer and thus solve a potential disposal problem.

In a hair pulping process, the hair protein is degraded to a soluble form. We have recovered protein from such effluents after first removing sulfide by oxidation. Acidification to a pH of 4.2 precipitated a protein product of 80% purity, reducing COD of the effluent by 70%. A yield of one pound of this protein was obtained from about 7.5 gallons of effluent from a hide processor (27,28). This protein is similar in composition to poultry feather meal. We are in the process of obtaining data to evaluate this product in animal feed.

We have recently undertaken studies on bio-oxidation with the aid of two relatively new tools. One of these is a carbon analyzer instrument that determines total organic carbon (TOC) of the effluent. It is a very rapid, reliable, and accurate procedure for analysis of oxidizable matter in waste water. COD and BOD are standard methods but are time consuming and much less precise. The TOC method is accurate to ±2% at the 50 mg. carbon/L level and determines all carbonaceous materials quantitatively in less than five minutes. It does not determine other oxidizable elemental forms such as sulfur or nitrogen, which also contribute to BOD of an effluent. Despite this we have found good correlation between TOC and COD of our unhairing effluents and have been using this technique to monitor the operation of our bio-reactor (29).

The newly developed technique of High Performance Liquid Chromatography (HPLC) was also applied in our studies on pollution control. A gel permeation chromatographic procedure that separated the unhairing effluent, in about one hour, into four fractions differing in molecular weight (i.e., greater than 5,000, 10,000, 50,000 and less than 100,000 apparent molecular weight) was developed. This method also gave an insight into the mechanisms of the bio-oxidation, during the course of which the two higher molecular weight fractions disappeared most rapidly and appeared to form lower molecular weight fragments (30).

Our Engineering group developed a continuous process for treating unhairing waste which permits recovery of products. In this process most of the suspended solids are first removed by flocculation. The supernatant is next acidified to a pH of 4 **in a closed system** to prevent escape of hydrogen sulfide (H_2S), an extremely toxic gas. The acidified stream is continuously pumped into a vacuum flash chamber where H_2S is flashed off and absorbed in sodium hydroxide solution, which is the sealing liquid inside a wet type vacuum pump. The acidulate contains precipitated protein, which is removed by filtration. By this process 92% of the lime and 73% of the fat are removed by flocculation, 68% of the protein is caught on the filter, and 80% or more of the sulfide is flashed off and recovered in three separate streams. The spent liquor contains principally water with residual amounts of unhairing components (31).

New Uses:

We are also doing research on new uses for hides and skins. Animal hides and skins are composed principally of the fibrous protein known as collagen, the basic raw material for leather, gelatin, and glue. New applications for collagen have been visualized and proposed; for example, as an extender and binder of meat, a source of animal protein for pet foods, a texturizing adjunct for vegetable proteins such as soy flour, a support medium for immobilizing enzymes, a wound dressing in the medical field, and an edible film for meat products and packaging. An interesting development in recent years was the commercial introduction of sausage casing based on collagen from cattlehide lime splits.

These new uses for collagen have been visualized because of its unique properties. Such uses require that the hide and skin be comminuted or dispersed without denaturation. For food use collagen must come from inspected slaughter, and identity with acceptable carcasses must be established.

Our laboratory developed a process for producing collagen dispersions (32,33) which was eventually studied on a small pilot plant scale. For our experimental work we obtained limed fresh splits from a tanner. The process for dispersing the collagen consists of six steps: washing the lime splits, precutting into strips, dicing the strips with a rotary knife cutter, deliming to the isoelectric point, comminuting in a cutting mill (Urschel Comitrol), and dispersion in a disc mill (shearing force). Five products differing in particle size were produced by varying the processing procedures (34). Food and pet food companies, fish farming institutions, cosmetic and pharmaceutical companies, universities, and researchers in enzyme immobilization have been interested in evaluting samples of these collagen dispersions.

Collagen offers considerable promise of becoming a food texturizing agent. Certain food elements such as soy flour, whey, dry milk powder, gums, and gelatin have been used with meat or meat analogues for economical or nutritional reasons. Textural deficiencies are commonly encountered in such blends. Incorporation of some collagen may overcome this deficiency.

Rat feeding experiments showed that the collagen preparations are completely digestible (35). However, collagen is a nutritionally incomplete protein. It contains no tryptophan and is deficient in all the other essential amino acids. Its protein efficiency ratio, a measure of the efficiency of weight gain, is low compared to caesin as a standard.

Improved Leathers:

Leather has been a preferred material for footwear for centuries. However, this does not mean that it can not be improved; it must be to meet the challenge of substitutes. Properties of leather that can be improved include: water resistance, perspiration resistance, scuff and abrasion resistance, colorfastness, launderability, drycleanability, flame retardance, oil resistance, heat resistance, self polishing, and last but not least, uniformity. Improving the product should return a premium to the tanner and benefit the livestock raiser, meat packer, hide dealer, and consumer.

Glutaraldehyde Tanning:

About 17 years ago our laboratory demonstrated the versatile tanning properties of glutaraldehyde and showed that it imparted desirable properties to the leather (36,37,38). Improved leathers resulted whether glutaraldehyde was used alone or preferably in combination with chrome or conventional tanning agents. Such versatility coupled with its availability at reasonable cost soon led to its commercial use in the leather industry in the U.S. Today glutaraldehyde is used in tanning many types of hides and skins but is most widely used by tanners producing side upper leather (39,40).

Glutaraldehyde improved the softness of the leather and its resistance to deterioration by perspiration and washing. It also gave some unexpected bonuses in the post tanning procesess such as improved uniformity in coloring, fat liquoring, sammying, and finishing (40).

Because of the washability and perspiration resistance of glutaraldehyde leather, we were interested in applying this tannage to shearlings, which were losing their markets as medical bedpads to synthetics. As expected, glutaraldehyde notably improved the shearlings so that this natural product recaptured some of its former markets. Today most shearling tanners produce a line tanned with glutaraldehyde and chrome that has found wide use in medical bedpads and other applications where comfort properties are important factors (41, 42,43).

Graft Polymerization:

New research offering considerable potential for improving leather involves the graft polymerization of vinyl monomers onto chrome leather. In practice, this would be similar to a retannage. In this process, a synthetic polymer is bonded chemically to the leather protein structure. This would be expected to impart new and improved properties to the leather. As much as 150% of synthetic polymer can be incorporate into the leather, but to retain the desirable characteristics of leather we prefer uptakes of about 25%. To date our best results have been obtained with methyl methacrylate and butyl acrylate as monomers for the graft copolymerization. The grafted copolymer exhibited some desirable properties such as: increased thickness, improved uniformity over the whole skin area, suppleness, retention of strength properties, water vapor permeability, and retention of the leather-like character (44,45,46).

We have studied the graft polymerization of butyl acrylate with a large variety of blue stock such as side upper, splits, calf, sheep, pig, and shearlings. Since this process can be considered analagous to a retannage, we have adopted the name PolyRetan Process to refer to this graft polymerization. The process is conducted in an oxygen free atmosphere using a persulfate-bisulfite redox system to initiate polymerization, which requires about four hours (47). Carbon dioxide, from dry ice or a cylinder, is convenient for sweeping oxygen from the head space of a drum or other tumbling device.

We have combined several operations (retan-color-fat liquor) into one retannage step, utilizing graft polyermization, polymerizable dyes, and an amphoteric surfactant as lubricant. The process was applied to sheepskin, pigskin, and shearlings, and resulted in leathers that were drycleanable. In the shearlings, grafting occurred more efficiently in the wool than in the skin (47). We plan to extend this work to garment leather from cowhide.

New Dyes:

Footwear is the principal outlet for leather. Garments offer considerable potential for expanding the market, although lack of easy care properties is a deterrent to their wider use. Fastness of dyes to drycleaning has aways posed a problem. We studied the use of some reactive dyes, principally Procion, Drimarene, and Remazol types, which are bonded chemically to the leather protein and are permanently fixed. The fastness of the dyed leather to washing, drycleaning, and perspiration was excellent (48,48).

New Lubricants:

We have also evaluated some amphoteric surfactants as novel lubricants for leather. These are long chain fatty derivatives of 8-amino-propionic acid (Deriphats) and of betaine (Lonzaine). Because these lubricants are only slightly soluble in drycleaning solvents, they are resistant to removal from leather on drycleaning (50,51).

Acknowledgement:

The work I have discussed was carried out by members of the Hides and Leather staff, both current and retired, as well as support personnel from other laboratories, too numerous to acknowledge individually. Their contributions have been recognized by leather scientists throughout the world. I would also like to acknowledge the cooperation of many in the tanning industry who generously contributed to our research effort.

I extend an invitation to all of you to visit our laboratory whenever you are in the Philadelphia area to discuss our research program and objectives for animal hides and skins in greater depth.

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